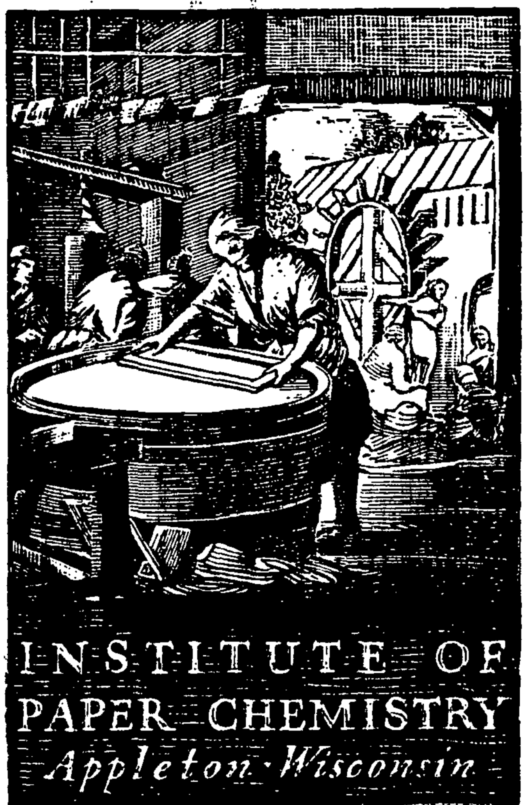

INVESTIGATION OF THE RELATIONSHIPS BETWEEN LIGNIN STRUCTURE AND ITS MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Ten

A Progress Report

to

PULP MANUFACTURERS RESEARCH LEAGUE

July 30, 1969

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SUMMARY

In pursuing studies in the adhesional phase of the program, a limited examination was made of the effects of reduced lignosulfonate surface tension on the bonding strength of southern pine plywood. The surface tension of electrodialyzed lignosulfonate (ELSA) was reduced from approximately 45 dynes/cm. to 34-35 dynes/cm. through incorporation of low levels of selected surface active agents. The low surface tension ELSA was utilized as the adhesive in preparing layups from veneer aged 2-3 weeks and having a critical surface tension of approximately 28 dynes/cm. A set of layup controls was prepared from "unmodified" ELSA which had been diluted to 37% solids in order to approach the solids and viscosity levels of the low surface tension materials. The bonding strength afforded by the low surface tension ELSA tended to be somewhat less than that provided by straight ELSA at 37% solids and this value, in turn, tended to be lower than that provided by 40% ELSA on the aged veneer. Cohesional failure using the low surface tension ELSA was estimated to be in excess of 95%. These results were interpreted in terms of preferential sorption of surfactant at the veneer — adhesive interface and in terms of reduced ELSA viscosity and increased penetration.

In the project area dealing with the cohesional strength of lignosulfonic acid adhesive materials for plywood, the use of lightweight paper for reeds for adhesive viscomechanical measurements was investigated, the measurement of the adhesive bond strength was established, and the correlation between loss tangent of the reed and the adhesive bond strength was observed.

As a means of increasing the sensitivity of the loss tangent of the reed to the behavior of the adhesive, lightweight papers were tested as substrates for the reeds. Under the usual conditions of ELSA adhesive cure, 310°F. at 150 p.s.i. for 30 min., kraft tissue (25 lb./TAPPI ream) cigarette paper, saturating rag stock (29 lb./TAPPI ream), glassine, and bleached kraft (45 lb./TAPPI ream) each became extensively charred and brittle making them useless for reed work. When the curing conditions were reduced to 310°, at 28 p.s.i. for 5 min. or 260°F. at 28 p.s.i. for 5 min., the 45-lb. bleached kraft paper was not seriously degraded. Layups were made with this substrate using the latter curing conditions. For comparison purposes, the adhesives previously used were employed. In addition, a similar set of layups was prepared using the previously employed substrate, 149 lb./TAPPI ream kraft, at curing conditions of 310°F. at 150 p.s.i. for 30 min. to be used for adhesive bond strength measurements.

The loss tangent data previously obtained showed a fairly high scatter, therefore a comparison was made between the rapid two-point method previously used and the slower, more precise frequency vs. vibrational amplitude method. Vibrational data were obtained by the two methods on two reeds cut from one of the layups. The precision by the latter method for measuring the resonance band width, $\Delta\omega$, was better so all subsequent loss tangent data were determined by this slower method. The scatter of the loss tangent data from different reeds in a layup is due primarily to the variability in the layup.

Loss tangent data were obtained on reeds from the 45-lb. bleached kraft layups including the substrate alone. The range of these data (0.041-0.047) was very small with an accuracy of up to ± 20%. Thus, the lighter weight substrate still has a major influence on the viscomechanical behavior of the reed.

Of the two methods considered for measuring the adhesive bond strength to shear stress, the method employing a specimen with a kerf in the lamina on each side at a prescribed distance apart was used because it does not require a gluing step and it is convenient. Six 1-inch square specimens were tested from each layup with the span between kerfs fixed by the strength of a lamina (1/32 in. for 45 lb. and 1/8 in. for 149 lb. paper). The deviation of the six specimens about the average was high (up to ± 50%), again primarily due to the variability in a layup. In both the 45-lb. bleached kraft layups and the 149-lb. kraft layups, the average bond strengths ranged from 100-1000 lb./in.^{2} Observations of the adhesive rupture zone showed that failure occurred in the region between the adhesive and the substrate indicating that the strength values represent lower limits of the cohesive strength of the adhesive.

Plots of loss tangent vs. bond strength showed that one increases with the other for the data from both the 45-lb. and the 149-lb. substrates. This correlation is apparent in spite of the large uncertainty of each datum and the limitation of the point of bond failure.

It is recommended that the program now focus on the cohesive strength properties of the adhesive isolated from the substrate. This will include the role of insolubilization on these properties.

ADHESIONAL PROPERTIES OF LIGNOSULFONIC ACIDS

INTRODUCTION

By way of review, in order for a liquid adhesive to form a strong bond with a solid surface, the chemical theory of adhesion requires that the liquid wet the solid surface with essentially a zero contact angle or, in other words, the attractive forces between the surface molecules of the adhesive film and the solid surface should be equal to, or greater than, the force of cohesion between the adhesive molecules themselves. These forces are frequently expressed in terms of surface tension and, in order to fulfill the aforementioned requirements, the surface tension of the adhesive must approach or equal the solid or critical surface tension (γ_c) of the adherend. The approach taken in the adhesional phase of the program has been one of measuring the liquid surface tension of ELSA and fractions thereof, the critical surface tension of southern pine veneer, and then relating these properties to the bonding strength of layups formed from the veneer utilizing unmodified ELSA and a formulated adhesive containing ELSA. Results given in Progress Report Nine revealed that the critical surface tension of the pine veneer declined as a function of aging at 73°F. and 50% R.H. reaching a level of approximately 28 dynes/cm. after two weeks. Subsequent bonding strength values utilizing the ELSA adhesives with liquid surface tensions of 44-45 dynes/cm. showed a tendency to decline as the veneer surface was aged prior to layup formation. Of the two adhesives, the formulated product provided substantially higher bonding strength and a much greater percentage of wood failure.

The present report describes results obtained to date in utilizing surface active agents to reduce the ELSA surface tension and promote adhesion. Theoretically, it would be necessary to reduce the ELSA surface tension to 28 dynes/cm. in order to provide complete wetting of the aged veneer surface. However, since the maximum work of adhesion usually occurs at low but finite contact angles and since Herczeg (1) found significantly reduced bonding strength when a surfactant was used to adjust the surface tension of a plywood adhesive below the critical surface tension of the veneer, it was decided to adjust the ELSA surface tension to 30-35 dynes/cm. for the present work.

EXPERIMENTAL

Lowering of ELSA Surface Tension

A total of seven commercial surfactants were examined for their effectiveness in lowering the surface tension of ELSA. These products were selected on the basis of available information concerning surface activity at low concentrations, stability in acid media, and foaming tendencies. A description of the agents is provided in Table I.

TABLE I

SURFACE ACTIVE AGENTS CONSIDERED FOR ADDITION TO ELSA

Product	Class or Composition	Type	Supplier
Triton QS-44	Phosphate ester	Anionic	Rohm & Haas Co.
Triton X-100	Octyl phenoxy polyethoxy ethanol	Nonionic	Rohm & Haas Co.
Igepal CO-610	Nonyl phenoxy polyethoxy ethanol	Nonionic	General Aniline & Film Corp.
Igepal CO-630	Same as Igepal CO-610	Nonionic	General Aniline & Film Corp.
FC-176	Fluorochemical	Nonionic	3M Co.
FC-134	Fluorochemical	Cationic	3M Co.
FC-173	Fluorochemical	Anionic	3M Co.

In an effort to conserve the supply of the reference ELSA (No. 66-2, Run 38), preliminary surface tension measurements were made in dilute sulfuric acid at pH 0.6, the pH of the unmodified ELSA. Stock solutions of all surfactants were prepared at a 0.1% active content in distilled water. This relatively low solids level was adopted because of the limited solubility of one of the fluorochemicals and because it afforded greater accuracy in preparing very low concentrations. The stock solutions were then utilized to prepare known concentrations in the range of 0.0001 to 0.05% in dilute sulfuric acid. The surface tension of the acid solutions was measured at 73°F. with a du Nouy Interfacial Tensiometer and the readings were adjusted for Harkins-Jordan correction factors (2). The results of these measurements are recorded in Table II. It was found, in the course of this work, that several of the fluorochemicals were adsorbed on glass and metal surfaces at low concentrations and, hence, fresh solutions of these agents were prepared in polyethylene beakers.

Based on the results in Table II, concentrations of surfactants were selected which provided a surface tension of 30-35 dynes/cm. However, when the specified amounts were incorporated into ELSA, the resulting surface tension was somewhat higher than anticipated, and therefore, increased amounts of surfactant were required to produce the desired surface tension level. The ELSA surface tension data are included in Table II and the surface tension — concentration relationships are shown graphically in Fig. 1.

Two sets of curves are apparent in Fig. 1; one for the fluorinated materials and the other for the nonfluorinated products. On the basis of the low surface tension provided by the fluorinated materials, it was decided to utilize these products and to include one nonfluorinated product in layup preparations.

TABLE II

THE SURFACE TENSION OF ELSA IN THE PRESENCE OF SELECTED SURFACTANTS

Surfactant	Concentration, %	Surface Tension, dynes/cm. In sulfuric acid at pH 0.6	In ELSA
Triton X-100	0.0050	40.5	--
	0.0080	--	43.9
	0.0100	33.0	--
	0.0320	--	39.7
	0.0500	31.5	--
	0.0800	--	35.3
Igepal CO-610	0.0010	39.8	--
	0.0025	33.2	--
	0.0050	32.0	45.9
	0.0100	31.4	44.2
	0.1000	--	36.6
Igepal CO-630	0.0010	44.5	--
	0.0020	36.5	--
	0.0050	32.2	--
	0.0100	32.0	--
	0.0400	--	40.7
	0.1000	--	37.0
	0.1500	--	34.7
FC-176	0.0025	31.7	39.5
	0.0050	20.2	34.5
	0.0100	20.1	31.6
FC-134	0.0001	70.4	--
	0.0005	23.7	--
	0.0010	22.4	44.2
	0.0050	--	35.7
	0.0100	--	29.0
FC-173	0.0010	52.7	44.2
	0.005	41.5	--
	0.0075	--	31.7
	0.0100	36.8	26.4
Triton QS-44	0.0010	45.7	--
	0.0050	36.7	--
	0.0100	32.9	44.4
	0.0200	--	42.5
	0.1000	--	36.0
	0.1200	--	34.4

Note: The surface tension values listed above represent the average of two determinations.

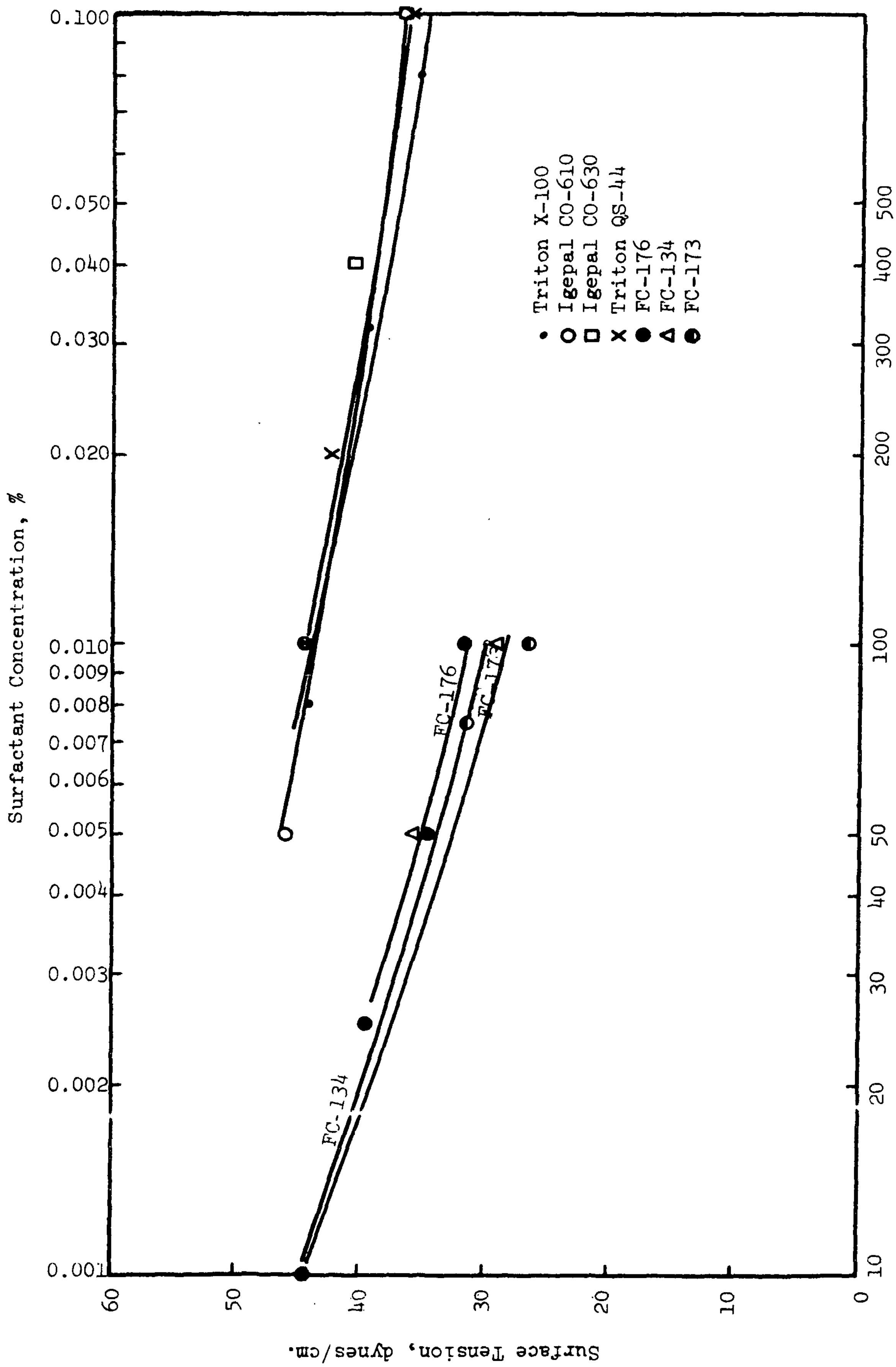


Figure 1. Surface Tension — Concentration Relationships for Selected Surfactants in ELSA

Preparation and Testing of Plywood Layups

Layups were prepared from hot-peeled clear southern pine veneer which had been sanded and then aged for 2-3 weeks at 73°F. and 50% R.H. The fluorochemicals were incorporated into unmodified ELSA to provide surfactant concentrations in the range of 0.006 to 0.009% (60-90 p.p.m.); Triton QS-44 was utilized at 0.12% (1200 p.p.m.). The surface tension of ELSA was measured immediately after blending in the surfactant and the adhesive was then used in preparing layups. Since incorporation of surfactant solutions reduced the effective ELSA concentration, a set of reference controls was included in which the ELSA was diluted to 37% solids with distilled water. The procedures used in preparing and testing the layups were identical to those described in Progress Report Nine. The bonding strength results along with pertinent surface tension and viscosity data are summarized in Table III. (Note: Table III includes results previously reported for freshly generated and aged surfaces.)

DISCUSSION OF RESULTS

It is readily apparent from the results in Table III that reducing the ELSA surface tension through incorporation of surfactants has, thus far, lead to reduced bonding strength. The reasons for this may be several. First of all, in spite of the low concentrations of surfactant used in three of four cases, these materials may have been preferentially sorbed at the veneer — adhesive interface causing a reduction rather than an increase in adhesion. As indicated earlier, there is evidence to suggest that some of the fluorinated materials are rapidly sorbed on solid surfaces. Secondly, incorporation of surfactants at low solids content reduced the effective concentration and viscosity of the ELSA, resulting in greater penetration into the wood. The role of viscosity on penetration is shown by the idealized rate of penetration equation

$$\frac{d\ell}{dt} = \frac{\gamma r \cos\theta}{4\eta\ell} \qquad (1)$$

FUTURE WORK

Laboratory work of immediate interest in the adhesional phase of the program will be concerned with the effects of increased ELSA viscosity on penetration and bonding strength in southern pine plywood. Increased viscosity may be achieved by increasing the solids content or by incorporating small percentages of selected polymers. In conjunction with this work it would also be desirable to examine further the effects of surface tension. One possibility which has not been explored involves enriching ELSA with the low molecular weight fraction previously found to be of low surface tension. The combination of higher viscosity and reduced surface tension should provide for moderate penetration and an adequate supply of ELSA to fill the surface voids.

MECHANICAL PROPERTIES OF LIGNOSULFONIC ACIDS

TRODUCTION

The ability of an adhesive to withstand an applied stress depends upon ress distribution within the adhesive. Internal stress redistribution is :complished through molecular relaxation, a property which is manifest in the .scomechanical behavior of the adhesive (3). The most convenient measure of ıis relaxation is the loss tangent, which is the ratio of energy lost to energy tored in a periodic application of stress (i.e., the ratio of the imaginary to ne real component of the complex modulus of the viscoelastic material).

It is the goal of the cohesional phase of this project to relate the iscomechanical properties of lignosulfonic acid materials to their adhesive trength, particularly in plywood operations. Greater understanding of the elationship will aid significantly the development of adhesive formulations.

Previous work (4) has shown that the potentially adaptable vibrating reed method of measuring viscomechanical properties of adhesives by means of their loss tangent, was possible when a porous substrate such as paper was used for the reed. This method allows the adhesive to be put through a normal curing process of high temperature and pressure. However, the limited sensitivity of the system to the loss tangent of the adhesive may have been caused by the heavy paper (149 lb./TAPPI ream) first examined.

The work presented in this report covers (1) the examination of lighter weight papers for reed substrates and the resultant loss tangent, (2) the measurement of the adhesive bond strength, and (3) the relationship between the loss tangent and the bond strength.

EXPERIMENTAL

Testing Lightweight Paper Substrates

The papers selected were tested by (1) immersing a 6 by 6-inch sheet in adhesive 65-24-R44 (a sodium-based, heat-treated ELSA with a concentration of 37% solids); (2) removing it after 5 min.; (3) plotting it gently; (4) placing it between 0.015-inch thick aluminum foil; and (5) putting this on heated platens at a selected temperature, pressure, and time to effect an adhesive cure. The conditions previously used (310°F. at 150 p.s.i. for 30 min.) were first tested but these were subsequently reduced to 310°F. at 28 p.s.i. for 5 min. and, likewise, to 260°F. at 28 p.s.i. for 5 min. After the curing period, the sheet was removed from the platens, cooled under conditions of 73°F. and 50% relative humidity, and examined for potential use in reed measurements. The following papers were examined:

(1) glassine
(2) bleached kraft M.F., 45 lb./TAPPI ream
(3) saturating rag stock, 29 lb./TAPPI ream
(4) cigarette paper
(5) kraft tissue, 25 lb./TAPPI ream.

Layups were made as previously described (4) using the 29 lb. rag stock and 45 lb. bleached kraft papers. A No. 8 Meyer rod was used with the above adhesive and the curing conditions were 260°F. at 28 p.s.i. for 5 min. to minimize substrate degradation.

Testing Methods of Measuring the Resonance Band Width, $\Delta\omega$

Two methods of measuring $\Delta\omega$ were described by Rieman and Kurath (5). (1) The two-point method involves measuring the vibrational amplitude at the resonance frequency, setting the traveling telescope at $1/\sqrt{2}$ times this maximum amplitude, and measuring the vibrational frequencies on either side of the resonance frequency which have this calculated amplitude. The difference in these frequencies is $\Delta\omega$. This is the method employed in this work up to the present time. (2) The amplitude *vs.* frequency method involves measuring the vibrational amplitude at a number of frequencies, plotting the amplitude *vs.* the frequency, and determining from the plot the difference in the frequencies, $\Delta\omega$, at $1/\sqrt{2}$ of the maximum amplitude. This second method is slower but potentially more accurate.

To compare these two methods, two 2.0 x 0.25-inch reeds were cut from the 45-lb. bleached kraft layup made using 65-25-R44 adhesive cured at 260°F. at 28 p.s.i. for 5 min. The vibrational measurements of the reeds were obtained as described in Progress Report Nine (*4*) by use of an audiooscillator coupled through an amplifier to a recording head (vibration transducer) with input voltage to the head held constant at 3.6 volts. The vibrational amplitude was measured by means of a traveling telescope.

Preparation of Layups

Layups, 6 by 6 inches in size, were prepared as described in Progress Report Nine (*4*) with the 45-lb. bleached kraft paper for substrate and curing conditions of 260°F. at 28 p.s.i. for 5 min., and also with the previously (*4*) used 149-lb. kraft liner board for substrate and curing conditions of 310°F. at 150 p.s.i. for 30 min. For reasons of comparison, the adhesives previously (*4*) employed were used, namely:

(1) 65-24-R44, a sodium-base, electrodialized, heat-treated whole liquor, 37% solids.

(2) Heat concentrated 65-24-R44, 38% solids.

(3) 67-36-R2, an ammonium-base, whole liquor, 39% solids.

(4) 66-2-R38, an ammonium-base, electrodialized, whole liquor, 40% solids. (For 30% solids the Brookfield viscosity at 25°C. and 12 r.p.m. is 4.0 centipoise.)

(5) Phenolformaldehyde resin, 50% solution, CR 9357, Catalin Corp. of America, Chicago, Illinois. (The Brookfield viscosity at 22°C. and 12 r.p.m. is 4.7 centipoise.)

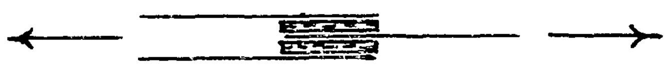
(6) Best formulation of Holderby, Olson, and Wegener (6); 30% ELSA solids (Sample 66-2-R38 used here) — 100 parts, 50% phenolformaldehyde — 24 parts, 200-mesh wood flour — 15 parts, freshly prepared and used immediately. (The Brookfield viscosity at 27°C. and 12 r.p.m. is 450 centipoise.)

In addition, layups were made using sulfuric acid of pH = 0.3 (a pH similar to the adhesive tested) as the "adhesive" for a control of the effect of acid on the substrate.

Reeds, 2.0 x 0.25 inch were cut from each layup as described in Progress Report Nine (4). Vibrational amplitude vs. frequency data were determined for reed numbers 1, 5, and 9 of the 45-lb. layups.

Measurement of Adhesive Bond Strength

Two methods were considered for measuring the adhesive bond strength to a shear force. The first method is to place equal size specimens glued symmetrically between three metal pulls, as:



so that stress applied to the pulls by means of the tensile tester (i.e., the Instron instrument) assures uniform shear stress to the specimens. The second method is to apply a tensile stress directly to a single specimen that has a kerf in the substrate on each side so that the cuts are parallel to each other while being perpendicular to the direction of stress and at a specific distance apart, as:

hus, the stress applied to the specimen by means of the tensile tester provide, to he adhesive region, a stress which is approximately a shear. The second method was elected as it does not involve the uncertain effects of gluing to pulls and, with care n cutting, it is conveniently applicable.

It would be most desirable to determine the bond strength of the actual eeds used for the vibration measurements. However, their narrow size precludes ither gluing or cutting, so that other specimens of each layup were tested for bond trength. Six specimens from each layup, 1.0 x 1.0 inch in size, were cut from the ide pieces remaining from the reed cutting operations. The kerf in the lamina on ach side of the specimen was made by placing the sample on a metal bar with a groove illed the width of the specimen and the depth of the thickness of a lamina (0.0035 nch for the 45-lb. bleached kraft and 0.007 inch for the 149-lb. kraft). A metal guide was placed on top of the sample and a kerf was made by carefully cutting the top amina with a new razor blade until the blade touched the top of the metal bar. The guide assures a straight cut perpendicular to the edge of the sample and at a set listance from the end of the sample. The sample was then turned over and the process repeated using a new razor blade and another metal guide to assure a fixed distance between kerfs. Some preliminary experiments were performed varying the distance between kerfs. If the kerfs were too far apart the specimen failed by breaking a lamina rather than by shear rupture of the adhesive region. For the 45-lb. bleached kraft the maximum useful distance between kerfs was found to be 1/32 inch and for the 149-lb. kraft it was 1/8 inch.

The specimen with kerfs was placed in line clamps of the Instron Tensile Tester and the stress was recorded while the sample was strained at the rate of 0.002 inch per min. until rupture occurred. The maximum stress is the adhesive bond strength The sample was then observed by means of a hand lens for the place of failure.

RESULTS AND DISCUSSION

In order to maximize the sensitivity of the loss tangent of the reed to the behavior of the adhesive, lightweight papers were examined as substrate for reeds. When the ELSA adhesive was cured at the usual conditions of 310°F. at 150 p.s.i. for 30 min., each of these papers was severely degraded as evidenced by becoming brittle and charred making reed work impossible. In the absence of ELSA, the papers were unaffected by these conditions, suggesting that the acid conditions are at fault. When the curing conditions for the ELSA were reduced to 310°F. at 28 p.s.i. for 5 min., the degradation of the 29-lb. rag stock and the 45-lb. bleached kraft was reduced. Likewise, by reducing the curing temperature to 260°F., substrate degradation for these two papers was further reduced, particularly for the 45-lb. bleached kraft, making reed work feasible. Subsequent layups were made with the 45-lb. bleached kraft paper and curing conditions of 260°F. at 28 p.s.i. for 5 min.

Since the precision of the resonance band width, $\Delta\omega$, measured by the two-point method is rather low (4), a comparison was made with $\Delta\omega$ measured by the more accurate vibrational amplitude *vs.* frequency method. A typical plot of these resonance peak data is shown in Fig. 2 and is similar to those given by Rieman and Kurath (5). The finite "amplitude" at the base line of the resonance peak is a result of the thickness of the reed. Table IV lists the results of resonance frequency, ω_o, and $\Delta\omega$ determined by the two different methods on two reeds cut from a layup made with 45-lb. bleached kraft, 65-24-R44 cured at 260°F. at 28 p.s.i. for 5 min. (See Appendix I for

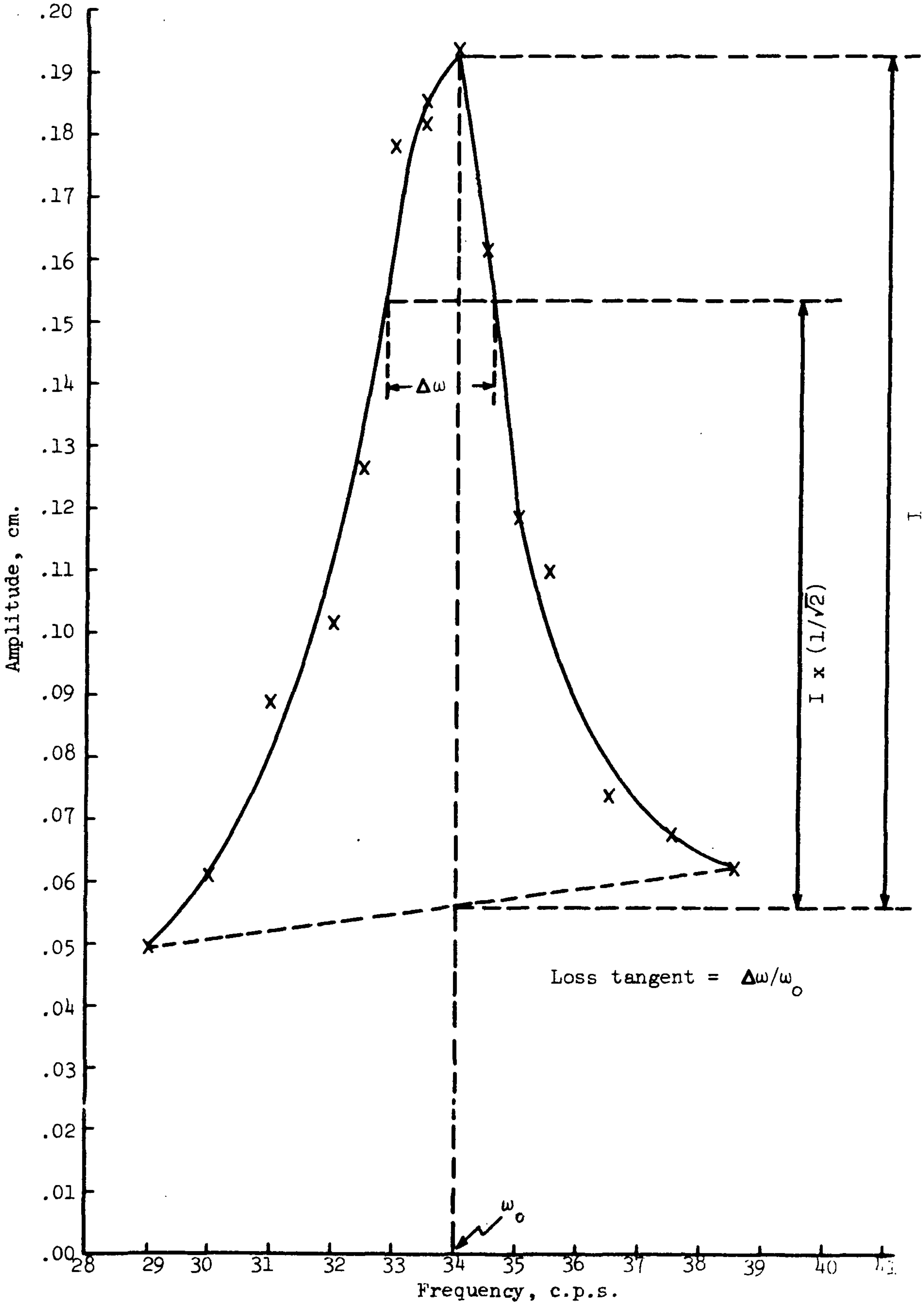


Figure 2. Vibrational Amplitude vs. Frequency for Reed No. 2

the basic data.) The amp. vs. freq. measurements were done twice on reed Number 1. The precision of $\Delta\omega$ by the amp. vs. freq. method was much better than by the two point method and the average values were somewhat different. However, the variation of the loss tangent between reeds is probably due to the variation of the regions in the layup. Measurements on the subsequent layups were made by the more precise but slower amp. vs. freq. method.

TABLE IV

COMPARISON OF METHODS FOR LOSS TANGENT MEASUREMENTS OF REEDS

Method	ω_o, c.p.s. Reed No. 1	ω_o, c.p.s. Reed No. 2	$\Delta\omega$, c.p.s. Reed No. 1	$\Delta\omega$, c.p.s. Reed No. 2	Loss Tangent, $\Delta\omega/\omega_o$ Reed No. 1	Loss Tangent, $\Delta\omega/\omega_o$ Reed No. 2
Two point	36.0	33.8	2.5, 1.8	2.5, 2.0	0.061	0.068
Amp. vs. Freq.	37.1 37.7	34.0	1.66 1.67	1.72	0.045 0.044	0.051

The adhesives previously tested (4) were examined again for comparison purposes using the 45-lb. bleached kraft paper for reed substrate. The loss tangent data of these systems are listed in Table V and the reed vibration data used to obtain these results are listed in Appendix I. The deviation about the average of the loss tangent data for three reeds from the same layup (up to ± 20%) is higher than the precision of a measurement for a single reed (< ± 10%). Thus, the deviation reflects the statistical variation of behavior within a layup. The range of average loss tangent data is very small, indicating that the loss tangent property of the reed with lightweight paper is still dominated by the substrate behavior. Since this 45-lb. paper was usable only with drastic reduction of curing conditions, in future work the adhesive will have to be isolated in order to improve the measurement of its loss tangent.

TABLE V

ADHESIVE BOND STRENGTH AND LOSS TANGENT DATA

Sample Identification			Bond Strength in Shear, lb./in. width							Loss Tangent			
			Specimen Readings							Reed Number			
Span	Substrata[a]	Adhesive[b]	1	2	3	4	5	6	av.	1	5	9	av.
1/32"	45 lb. bl. kraft	R-44 W.L.	5.8	7.8	2.2	1.7	6.6	8.7	5.5	.047	.057	.046, .039	.047
"	"	R-44 conc.	1.5	3.3	2.8	2.7	3.3	5.4	3.2	.035	.044	.044	.041
"	"	R-38	6.7	3.4	3.5	5.3	8.6	--	5.5	.042	.042	.048	.044
"	"	R-2	27.5	11.5	16.2	40.0	38.0	--	29.9	.043	.054	.044	.047
"	"	Phenol	4.5	7.1	10.1	3.6	--	--	6.3	.051	.044	.042	.046
"	"	Formulation	24.0	23.0	21.0	16.5	17.5	18.0	20.0	.048	.047	.047	.047
--	"	None	--	--	--	--	--	--	--	.043	.040	.059	.047
1/8"	149 lb. unbl. kraft	Phenol	109.0	46.0	125.0	104.0	88.0	111.0	97.2	--	--	--	.050[c]
"	"	R-2	23.5	56.0	51.0	26.0	50.0	--	41.3	--	--	--	.034
"	"	Formulation	50.0	62.0	26.0	77.0	29.0	20.0	44.0	--	--	--	.045
"	"	R-38	37.5	14.0	16.3	7.7	50.0	33.3	26.5	--	--	--	.038
"	"	R-44 conc.	60.9	21.2	43.2	47.5	60.7	54.5	48.0	--	--	--	.041
"	"	R-44, W. L.	58.1	24.8	20.7	26.6	37.7	33.2	33.5	--	--	--	.025
"	"	H_2SO_4	11.0	16.0	12.7	8.3	17.1	--	13.0	--	--	--	--
--	"	None	--	--	--	--	--	--	--	--	--	--	.024

[a]The 45-lb. bleached kraft paper system was cured at 260°F. for 5 min. at 28 p.s.i. and the 149-lb. kraft paper system was cured at 310°F. for 30 min. at 150 p.s.i.

[b]The adhesive descriptions are given on p. 15.

[c]The loss tangent averages for the 149-lb. kraft system are based on samples previously reported in Progress Report Nine (4).

The adhesive bond strength in shear stress of these 45-lb. layups and of 149-lb. layups with the same adhesives but cured at the usual conditions of 310°F. at 150 p.s.i. for 30 min., are listed in Table V. The 149-lb. layups are a duplication of those reported in Progress Report Nine (4) for which two-point method loss tangent data are thus available for correlation assessments. The deviation from the average bond strength (up to ± 50%) is high reflecting the variable behavior within a layup. When placed on a unit area basis, the two sets of layups fall in the same range (100-1000 lb./in.^{2}). It is interesting to note that the usually good adhesive, phenol-formaldehyde, has a low bonding value for the 45-lb. paper. This unexpected result may be due to the low curing pressure and temperature (28 p.s.i. and 260°F. compared to the more favorable 150 p.s.i. and 310°F. used with the 149-lb. paper). This would limit the penetration of the adhesive into the substrate, thus reducing mechanical bonding. It is also interesting to note that sulfuric acid, pH = 0.3, alone caused some bonding of the 149-lb. paper, possibly through moisture effects and/or charring reactions.

Microscopic observations of the rupture zone in all cases showed that failure occurred in the region between the adhesive and the substrate. The exposed adhesive interface always contained scattered fibers and the adhesive appeared to be within a discrete layer (this would probably not be the case on a more porous wood surface). Since the bond failure was not within the adhesive layer, the strength data represent minimum values of the cohesive strength of the adhesives.

Plotted in Fig. 3 and 4 are the loss tangent *vs*. bond strength data for the 45-lb. bleached kraft layups and the 149-lb. kraft layups, respectively. In spite of the large uncertainty of each datum and the limitation of the point of bond failure, there seems to be a correlation of the loss tangent and adhesive bond

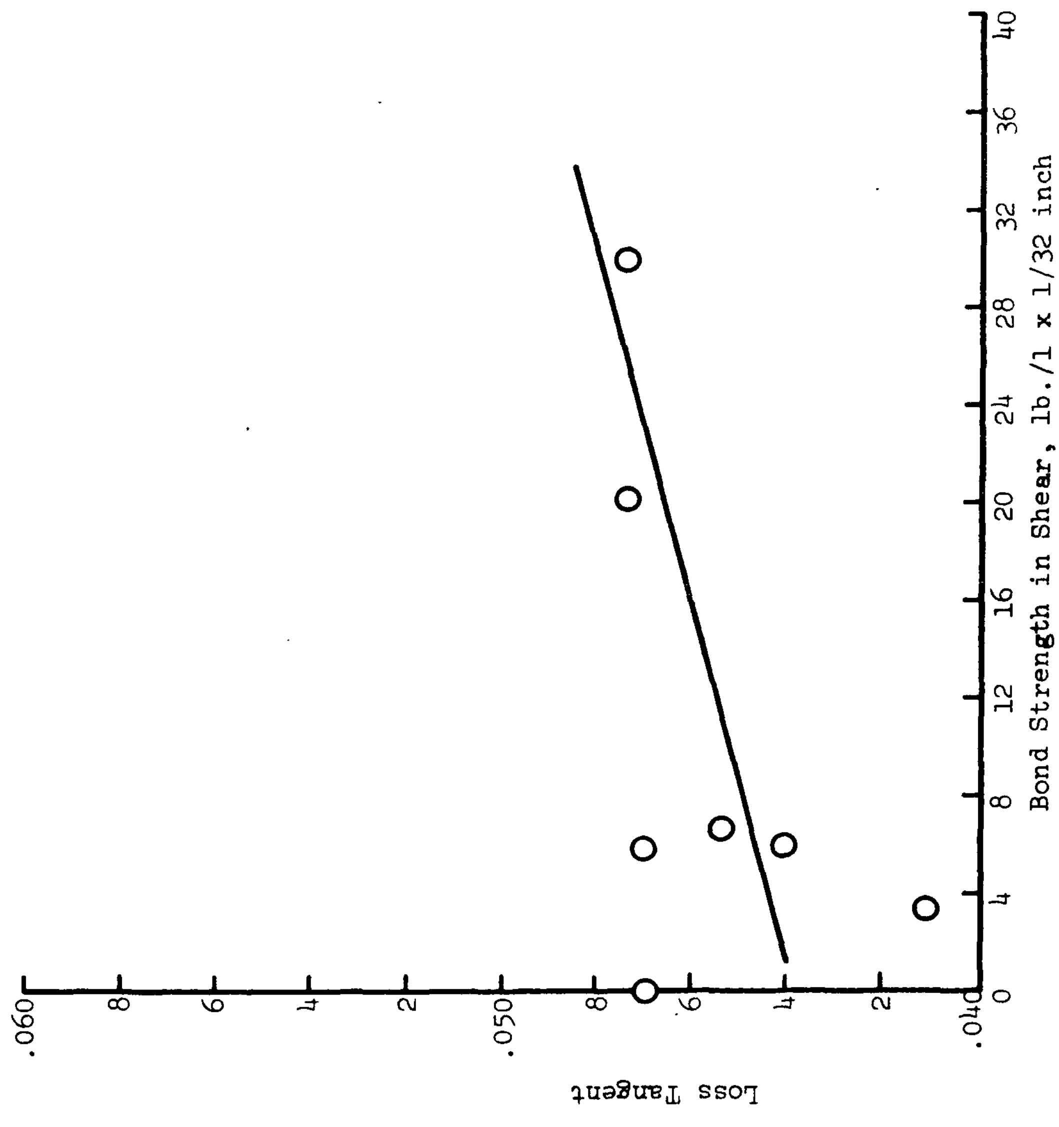


Figure 3. Loss Tangent *vs.* Bond Strength for 45 lb./Ream Bleached Kraft, Cured at 260°F. for 5 min. at 28 p.s.i.

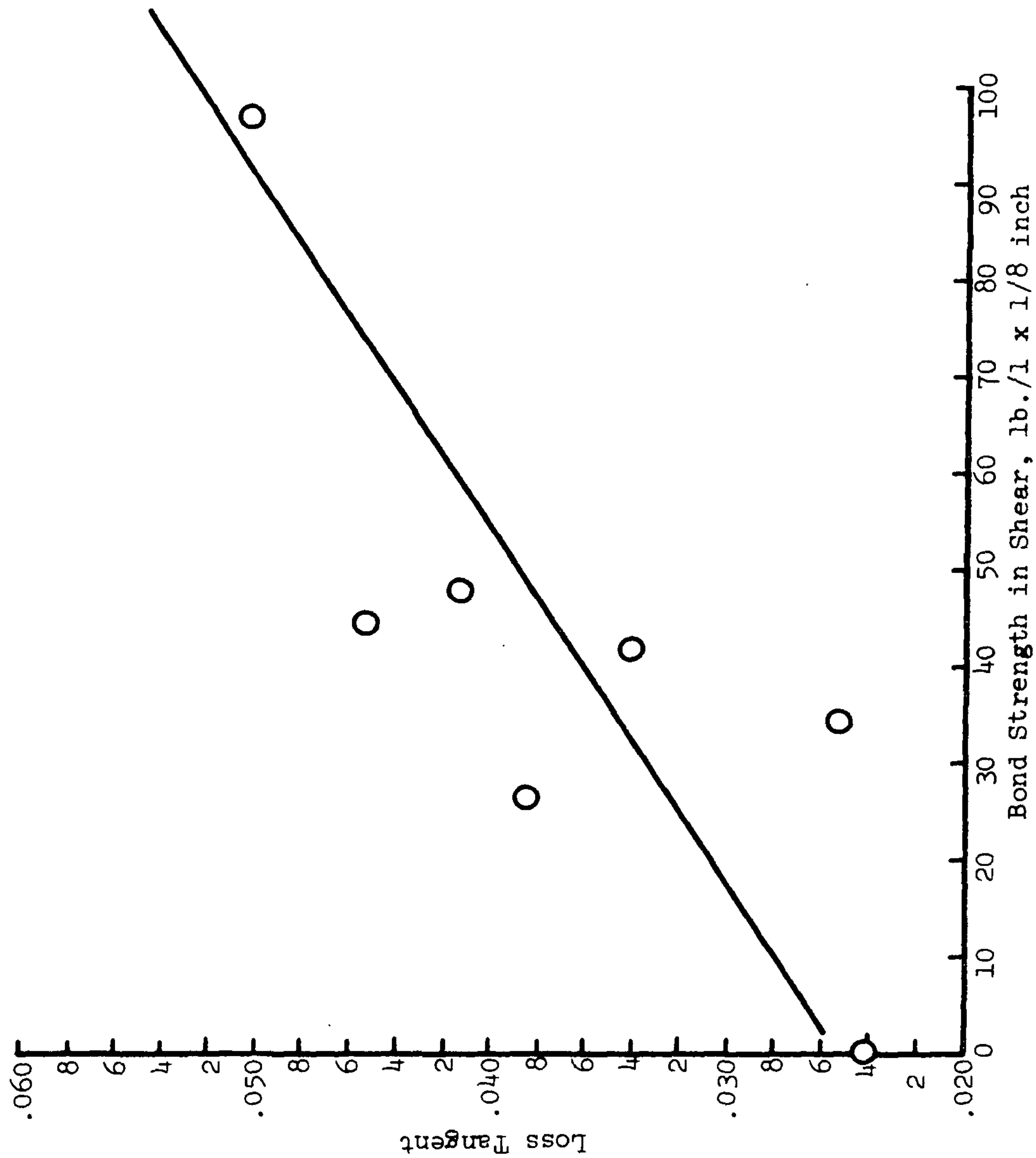


Figure 4. Loss Tangent vs. Bond Strength for 149 lb/Ream Kraft, Cured at 310°F. at 150 p.s.i. for 30 min.

strength, one increasing with the other. The loss tangent is thus a potentially useful parameter in studies of adhesive behavior.

FUTURE WORK

Because of (1) the large scatter of the loss tangent and strength data of the bonded system due to the heterogeneity of the wood or paper substrate, and (2) the bond failure commonly observed to be in the substrate, it is recommended that the program now focus on the cohesive strength properties of the adhesive isolated from the substrate. Such a focus could also include the role of insolubilization which has never been measured but which is ultimately important in testing the adhesive.

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APPENDIX I

BASIC DATA ON THE LAYUPS AND THE VIBRATING REEDS

The basic data on the layups using the 45-lb. bleached kraft paper with ıe adhesive cured at 260°F. at 28 p.s.i. for 5 min., and on the layups using the ı9-lb. kraft paper with the adhesive cured at 310°F. at 150 p.s.i. for 30 min. are .ven in Table VI. The basic vibrating reed data from these 45-lb. bleached kraft ıper layups are given in Table VII and the resulting data needed to calculate the ɔss tangents are given in Table VIII.

TABLE VI

DATA ON THE LAYUPS

Adhesive Type[a]	Adhesive Concn., % solid	6x6-Inch Two Ply, uncoated	Layup Weight, g. coated	Adhesive Weight, g.	Coating Rod
45 lb./TAPPI Ream Bleached Kraft					
65-24-R44[b]	37.0	3.0111	3.2192	0.2081	Mayer No. 8
65-24-R44	37.0	3.0000	3.4311	0.4311	Mayer No. 12
65-24-R44, concentrated	38.7	2.9770	3.4427	0.4657	Mayer No. 10
66-2-R38	30.0	3.0264	3.428	0.4018	Mayer No. 12
67-36-R2	39.1	3.0422	3.5498	0.5076	Mayer No. 10
Phenol-formaldehyde	50.0	3.0369	3.5541	0.5172	Mayer No. 8
Formulation H_2SO_4	0.3M	3.0332	3.0064	(0.0268)	Mayer No. 8
149 lb./TAPPI Ream Kraft					
Phenol-formaldehyde	50.0	9.6982	10.2900	0.5918	Mayer No. 8
67-36-R2	39.1	9.7144	10.0567	0.3423	Mayer No. 10
Formulation	Approx. 40.0	9.7343	10.2290	0.4947	Mayer No. 14
66-2-R38	30.0	9.7150	10.1342	0.4192	Mayer No. 12
65-24-R44 concentrated	38.7	9.6695	9.8950	0.2255	Mayer No. 10
65-24-R44 whole liquor	30.0	9.7761	9.9160	0.1399	Mayer No. 12
H_2SO_4	0.3M	9.7876	9.0534	(0.7342)	Mayer No. 8

[a]See p. 15 for descriptions.
[b]This layup was used to make the reeds for the comparison of $\Delta\omega$ methods.

TABLE VII

DATA ON THE VIBRATING REEDS FROM 45-LB. BLEACHED KRAFT PAPER

65-24-R44[a]

Reed No. 1		Reed No. 1 (rerun)		Reed No. 2	
Freq., c.p.s.	Amp., cm.	Freq., c.p.s.	Amp., cm.	Freq., c.p.s.	Amp., cm.
37.0	0.1929	37.7	0.2196	33.5	0.1851
37.5	0.1869	38.2	0.1980	34.0	0.1934
38.0	0.1680	38.7	0.1799	34.5	0.1612
38.5	0.1468	39.2	0.1354	35.0	0.1182
39.0	0.1122	40.0	0.0990	35.5	0.1096
40.0	0.0861	41.0	0.0845	36.5	0.0737
41.0	0.0696	42.0	0.0801	37.5	0.0670
37.0	0.2008	37.5	0.2119	38.5	0.0616
36.5	0.1549	37.0	0.1771	33.5	0.1815
36.0	0.1192	36.5	0.1350	33.0	0.1783
35.5	0.1096	36.0	0.1154	32.5	0.1263
35.0	0.0839	35.0	0.0845	32.0	0.1013
34.0	0.0735	34.0	0.0811	31.0	0.0888
33.0	0.0662	33.0	0.0719	30.0	0.0608
				29.0	0.0496

Reed No. 1		Reed No. 5		Reed No. 9 (rerun)	
33.6	0.1861	38.9	0.1839	38.1	0.1976
34.1	0.1788	38.4	0.1670	38.6	0.1991
34.6	0.1569	37.9	0.1453	39.1	0.1651
35.1	0.1371	37.4	0.1297	39.6	0.1587
35.6	0.1143	36.9	0.1083	40.1	0.1281
36.1	0.1079	36.4	0.1008	40.6	0.1106
36.6	0.0848	35.9	0.0951	41.1	0.1004
33.7	0.1720	39.4	0.1860	38.0	0.2197
33.2	0.1611	39.9	0.1782	37.5	0.1984
32.7	0.1235	40.4	0.1577	37.0	0.1471
32.2	0.0980	40.9	0.1383	36.5	0.1361
31.7	0.0909	41.4	0.1207	36.0	0.1204
31.2	0.0815	41.9	0.1179	35.5	0.1099
30.7	0.0748	42.4	0.1030	35.0	0.0970

65-24-R44 Concentrated

Reed No. 1		Reed No. 5		Reed No. 9	
34.0	0.2216	36.2	0.1934	34.2	0.2098
33.5	0.1887	35.7	0.1822	34.7	0.1956
33.0	0.1526	35.2	0.1366	35.2	0.1827
32.5	0.1355	34.7	0.1154	35.7	0.1444
32.0	0.1120	34.2	0.1012	36.2	0.1160
31.5	0.1027	33.7	0.0884	36.7	0.0969
31.0	0.0983	33.2	0.0896	37.2	0.0894
34.2	0.2284	36.2	0.2047	34.2	0.2064
34.7	0.1920	36.7	0.1944	33.7	0.1665
35.2	0.1692	37.2	0.1684	33.2	0.1320
35.7	0.1432	37.7	0.1292	32.7	0.1143
36.2	0.1198	38.2	0.1074	32.2	0.0987
36.7	0.1124	38.7	0.1022	31.7	0.0958
37.2	0.1022	39.2	0.0902	31.2	0.0907

66-2-R38

Reed No. 1		Reed No. 5		Reed No. 9	
33.3	0.2015	35.7	0.2058	36.0	0.2199
33.8	0.2096	36.2	0.1973	36.5	0.1974
34.3	0.1743	36.7	0.1668	37.0	0.1585
34.8	0.1383	37.2	0.1306	37.5	0.1286
35.3	0.1182	37.7	0.1126	38.0	0.1108
35.8	0.1065	38.2	0.1045	38.5	0.1000
36.3	0.0923	38.7	0.0902	39.0	0.0830
33.3	0.2228	35.7	0.2125	36.0	0.2232
32.8	0.1882	35.2	0.1850	35.5	0.2245
32.3	0.1308	34.7	0.1489	35.0	0.1821
31.8	0.1222	34.2	0.1182	34.5	0.1519
31.3	0.1011	33.7	0.997	34.0	0.1106
30.8	0.0870	33.2	0.0888	33.5	0.1039
30.3	0.0875	32.7	0.0813	33.0	0.1000

[a]These reeds were used for the comparison of the $\Delta\omega$ method.

TABLE VII (Continued)

DATA ON THE VIBRATING REEDS FROM 45-LB. BLEACHED KRAFT PAPER

67-36-R2

Reed No. 1		Reed No. 5		Reed No. 9	
Freq., c.p.s.	Amp., cm.	Freq., c.p.s.	Amp., cm.	Freq., c.p.s.	Amp., cm.
35.6	0.1984	37.0	0.1999	35.6	0.2027
36.1	0.1871	37.5	0.1761	35.1	0.1660
36.6	0.1600	38.0	0.1629	34.6	0.1350
37.1	0.1282	38.5	0.1269	34.1	0.1051
37.6	0.1045	39.0	0.1040	33.6	0.0930
38.1	0.0902	39.5	0.0991	33.1	0.0844
38.6	0.0799	40.0	0.0875	32.6	0.0757
35.6	0.1891	37.0	0.1953	35.6	0.2036
35.1	0.1635	36.5	0.1982	36.1	0.1985
34.6	0.1306	36.0	0.1662	36.6	0.1812
34.1	0.0949	35.5	0.1340	37.1	0.1389
33.6	0.0821	35.0	0.1118	37.6	0.1137
33.1	0.0715	34.5	0.1011	38.1	0.0979
32.6	0.0718	34.0	0.0892	38.6	0.0888

Phenolformaldehyde

Reed No. 1		Reed No. 2		Reed No. 6	
37.5	0.1627	35.4	0.1971	42.6	0.2156
37.0	0.1325	34.9	0.1901	42.1	0.1922
36.5	0.1072	34.4	0.1579	41.6	0.1648
36.0	0.0896	33.9	0.1149	41.1	0.1159
35.5	0.0762	33.4	0.0905	40.6	0.1130
35.0	0.0724	32.9	0.0849	40.1	0.0914
34.5	0.0637	32.4	0.0772	39.6	0.0945
38.2	0.1695	35.4	0.2001	42.6	0.2190
38.7	0.1585	35.9	0.1843	43.1	0.2131
39.2	0.1350	36.4	0.1399	43.6	0.1795
39.7	0.1124	36.9	0.1132	44.1	0.1627
40.2	0.0956	37.4	0.0936	44.6	0.1388
40.7	0.0823	37.9	0.0753	45.1	0.1151
41.2	0.0816	38.4	0.0716	45.6	0.1053

Formulation

Reed No. 1		Reed No. 5		Reed No. 9	
33.7	0.1941	32.7	0.1882	33.6	0.1806
33.2	0.1554	32.2	0.1685	33.1	0.1888
32.7	0.1216	31.7	0.1159	32.6	0.1401
32.2	0.1057	31.2	0.0861	32.1	0.1103
31.7	0.0963	30.7	0.0806	31.6	0.0924
31.2	0.0887	30.2	0.0671	31.1	0.0723
30.7	0.0802	29.7	0.0663	30.6	0.0743
34.2	0.2126	32.7	0.1679	33.7	0.1951
34.7	0.1950	33.2	0.1728	34.2	0.1621
35.2	0.1533	33.7	0.1388	34.7	0.1107
35.7	0.1145	34.2	0.0990	35.2	0.1054
36.2	0.0954	34.7	0.0834	35.7	0.0826
36.7	0.0935	35.2	0.0736	36.2	0.0767
39.2	0.0834	35.7	0.0744	36.7	0.0714

No Adhesive, Single Lamina

Reed No. 1		Reed No. 5		Reed No. 9	
21.2	0.1454	20.0	0.1480	19.9	0.1485
21.0	0.1408	19.8	0.1391	19.7	0.1243
20.8	0.1241	19.6	0.1234	19.5	0.1196
20.6	0.1137	19.4	0.1038	19.3	0.1034
20.4	0.1065	19.2	0.0895	19.1	0.0876
20.0	0.0761	18.9	0.0754	18.7	0.0717
19.6	0.0705	18.5	0.0684	18.3	0.0561
21.2	0.1504	20.0	0.1483	19.9	0.1310
21.4	0.1382	20.2	0.1375	20.1	0.1378
21.6	0.1264	20.4	0.1276	20.3	0.1324
21.8	0.1226	20.6	0.1155	20.5	0.1271
22.0	0.0961	20.8	0.1035	20.7	0.1163
22.4	0.0756	21.2	0.0851	21.1	0.1010
22.8	0.0671	21.6	0.0769	21.5	0.0788

TABLE VIII

DATA FROM FREQ. VS. AMP. FOR DETERMINING LOSS TANGENT
WITH 45-LB./TAPPI REAM REEDS

Adhesive	Reed No.	Base Line, cm.	ω_o, c.p.s.	Amplitude I, cm.	Ix $(1/\sqrt{2})$	Amplitude Location of $\Delta\omega$, cm.	$\Delta\omega$ c.p.s.	$\Delta\omega/\omega_o$, Loss Tangent
65-24-R44 whole liquor	1	0.0799	33.8	0.1039	0.0735	0.1534	1.57	0.0465
	5	0.0992	39.4	0.0868	0.0614	0.0614	2.25	0.0571
	9	0.0990	38.0	0.1080	0.0764	0.1754	1.73	0.0455
65-24-R44 concentrated	1	0.1003	34.2	0.1282	0.0907	0.1910	1.21	0.0354
	5	0.0898	36.25	0.1121	0.0793	0.1691	1.60	0.0441
	9	0.0900	34.20	0.1198	0.0847	0.1747	1.50	0.0439
66-2-R38	1	0.0894	33.22	0.1304	0.0922	0.1816	1.41	0.0424
	5	0.0860	35.70	0.1236	0.0874	0.1734	1.51	0.0423
	9	0.0925	35.70	0.1311	0.0927	0.1852	1.70	0.0476
67-36-R2	1	0.0756	35.78	0.1213	0.0858	0.1614	1.55	0.0433
	5	0.0883	36.87	0.1097	0.0776	0.1659	2.00	0.0543
	9	0.0822	35.60	0.1206	0.0853	0.1675	1.58	0.0444
Phenol-formaldehyde	1	0.0734	38.20	0.0963	0.0681	0.1415	1.95	0.0511
	2	0.0740	35.40	0.1252	0.0885	0.1625	1.55	0.0438
	6	0.0982	42.6	0.1191	0.0842	0.1824	1.77	0.0416
Formulation	1	0.0820	34.2	0.1305	0.0923	0.1743	1.65	0.0483
	5	0.0703	32.7	0.1178	0.0833	0.1538	1.52	0.0465
	9	0.0720	33.5	0.1190	0.0842	0.1562	1.58	0.0472
Single ply 45-lb. bl. kraft, no adh.	1	0.0689	21.2	0.0786	0.0556	0.1245	0.92	0.0434
	5	0.0723	20.0	0.0759	0.0537	0.1260	0.80	0.0400
	9	0.0683	19.98	0.0731	0.0517	0.1200	0.117	0.0586
65-24-R44 whole liquor	9 Rerun	0.0992	38.75	0.1000	0.0707	0.1699	1.50	0.0387